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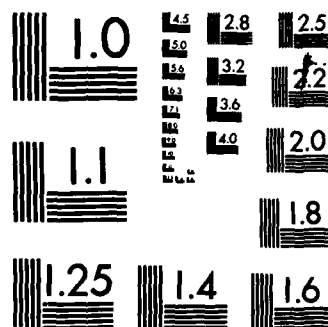
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Molecular Orbital Study of Acyclical Nitramine Compounds

G. H. HERLING

*Radiation-Matter Interactions Branch
Condensed Matter and Radiation Sciences Division*

September 25, 1985



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Molecular Orbital Study of Acyclical Nitramine Compounds

I. INTRODUCTION

Nitramines (nitro-amines) are chemical compounds which have the generic structure shown in Fig. 1. There is a nitro group, NO_2 , double bonded to a nitrogen atom, while the moieties X and Y, which may be members of a ring or radicals, complete the amine structure; a resonance structure for the N-O bonds is understood.

Such compounds are of both theoretical and experimental interest because a number of them are explosive, while others may serve as models of explosives. Figure 2 contains the structures of the explosive RDX, and the model compound dimethylnitramine (DMNA). The 1, 2, 6 positions of RDX, shown above the dashed line, are modeled by the part of DMNA above that line. The moieties X and Y correspond to the CH_2 carbenes in both RDX and DMNA. In the former, they are members of the ring; in the latter, they combine with the remaining H atoms to form the CH_3 methyl radicals.

Cont'd

Because the reactions of such molecules are complicated, it may happen that the first steps of their decompositions are not amenable to experimental study, and, in order to attempt to obtain an understanding of the complete dynamics, it is necessary to perform theoretical calculations. The small value of the ratio of electron to proton masses, $1/1823$, leads to a decoupling of the electronic motion from that of the heavy particles, the Born-Oppenheimer approximation. The quantum mechanical treatment of the electronic motion for fixed positions of the nuclei forms the basis of quantum chemistry which generates a potential energy surface that determines

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the heavy particle motion classically, semi-classically, or quantum mechanically,

In Sec II, the Hartree-Fock (HF) self-consistent field (SCF) method is briefly described. It underlies, in some fashion, all forms of quantum chemistry. The reduction of the HF equations by means of atomic orbitals (AO's) is described as is the problem of multifold proliferation of matrix elements. In Sec. III, the reduction of the full SCF Hamiltonian to the MINDO/3² and MNDO^{3,4} forms is discussed, and the empirical parameterization of matrix elements is described. In Sec. IV, the results obtained for the ground state properties of several acyclical nitramine compounds using the MINDO/3 and MNDO Hamiltonians are compared with each other and with experiment. Conclusions are contained in Sec. V.

II. THE SELF-CONSISTENT FIELD-LINEAR COMBINATION OF ATOMIC ORBITALS-MOLECULAR ORBITAL (SCF-LCAO-MO) METHOD

The complete non-relativistic molecular Hamiltonian may be written as

$$H = \sum_{\alpha} T_{\alpha} + \sum_{\alpha > \beta} V_{\alpha\beta} + \sum_i T_i + \sum_{i, \alpha} V_{i\alpha} + \sum_{i > j} V_{ij}, \quad (1)$$

where the sum on Greek indices goes over the atomic nuclei and that on Latin indices goes over the electrons. The quantities T are the kinetic energies and the symbols V denote the Coulomb potential energies. In terms of natural units such that

$$\hbar = m_e = |e| = 1,$$

Eq (1) acquires the form

$$H = (1/M_A) \sum_{\alpha} (P_{\alpha}^2 / 2A_{\alpha}) + \sum_{\alpha > \beta} Z_{\alpha} Z_{\beta} |\vec{R}_{\alpha} - \vec{R}_{\beta}|^{-1} \\ + \sum_i (p_i^2 / 2) - \sum_{i, \alpha} Z_{\alpha} |\vec{r}_i - \vec{R}_{\alpha}|^{-1} + \sum_{i > j} |\vec{r}_i - \vec{r}_j|^{-1}, \quad (1.1)$$

where the quantities $p(P)$ are the momenta, the quantities Z the atomic numbers, the nuclear masses in atomic mass units are A_{α} , while \vec{R} and \vec{r} denote the positions of the corresponding particles. The occurrence of the factor $M_A^{-1} = (1/1823)$, the inverse of the atomic mass unit expressed in natural units, suggests the Born-Oppenheimer approximation, the consideration of Eq. (1.1) for fixed positions of the nuclei. Treating the nuclear coordinates as parameters leads to the fundamental equation of quantum chemistry

$$H_e(\vec{r}, \vec{R}) \psi_m(\vec{r}, \vec{R}) = U_m(\vec{R}) \psi_m(\vec{r}, \vec{R}), \quad (2)$$

where \vec{r} and \vec{R} denote all of the \vec{r}_i and \vec{R}_{α} , respectively and

$$H_e(\vec{r}, \vec{R}) = -\sum_i (\nabla_i^2 / 2) + \sum_{\alpha} Z_{\alpha} |\vec{r}_i - \vec{R}_{\alpha}|^{-1} \\ + \sum_{i > j} |\vec{r}_i - \vec{r}_j|^{-1} + \sum_{\alpha > \beta} Z_{\alpha} Z_{\beta} |\vec{R}_{\alpha} - \vec{R}_{\beta}|^{-1}. \quad (3)$$

The functions $\psi_m(\vec{r}, \vec{R})$ which diagonalize Eq. (2) are adiabatic basis functions, and the eigenvalues $U_m(\vec{R})$ are adiabatic electronic energies. In order to solve the complete problem implied by Eq. (1), non-adiabatic correction terms must be added to the potential U_m in order to obtain a solution for the nuclear part of the total wave function. Alternatively, one may choose to define electronic energies as the eigenvalues of a Hamiltonian other than that given by Eq. (3) in which case the functions corresponding to the ψ_m are known as diabatic basis functions, and the eigenvalues as diabatic potential energy surfaces.

The variational method supplies a means of constructing approximate solutions of Eq. (2) according to the prescription that the energy functional

$$U_m(\vec{R}, \psi_m) \equiv \frac{\langle \psi_m | H_e | \psi_m \rangle}{\langle \psi_m | \psi_m \rangle} \quad (4)$$

be stationary with respect to variations of the functions $|\psi_m\rangle$ (or $\langle\psi_m|$) subject to the subsidiary condition

$$\langle \psi_m | \psi_m \rangle = 1 .$$

The variational method becomes the HF method when the $|\psi_m\rangle$ are restricted to be single Slater determinants composed of one electron spin-orbital functions. For the ground state of a closed shell system of N electrons, it is convenient to suppress the subscript m and write $|\psi_m\rangle$ in the form

$$|\psi\rangle = (N!)^{-1/2} \sum_P (-)^P \prod_{i=1}^N \eta_i |\phi_i\rangle , \quad (5)$$

where the η_i assume the values α_i or β_i according to the z -component of the spin of the i^{th} electron. The $|\phi_i\rangle$ are a set of single particle orbitals, and the sum extends over the permutations P of parity $(-)^P$ that may be formed from the product given in a standard order. Because the resulting equations are non-linear, they are solved by iteration until convergence of two (or more) consecutive iterations to within a given tolerance is achieved, i.e., the solution is self-consistent and the resulting energy is said to have been calculated by the HF-SCF method. The method becomes the HF-SCF-LCAO-MO method if a linear combination of atomic orbitals (LCAO) centered on the nuclei α are chosen for the molecular orbitals (MO) $|\phi_i\rangle$ in which case

$$|\phi_i\rangle = \sum_{p=1}^k \chi_p C_{pi} \quad 1 \leq i \leq N/2 . \quad (6)$$

The index $p \equiv (\alpha, \lambda)$ where λ labels the atomic orbitals centered on the nucleus α , and the $|\chi_p\rangle$ are the normalized atomic orbitals. The upper limit to the sum, K , has a value not less than $N/2$. If it were allowed to be infinite, the $|\phi_i\rangle$ would be a complete set, and the solution of Eq. (4) would be at the HF limit. If K were to correspond to the minimal number of functions needed to describe the valence electrons, is for H and $2s$, $2p_x$, $2p_y$ and $2p_z$ for first row atoms, the basis set is minimal. A minimal basis set is employed in the calculations to be discussed.

The definition (6) does not imply that the $|\phi_i\rangle$ form an orthonormal set, but a unitary transformation enables them to be written as such. The variation of the anti-symmetrized product may be written as a variation of the C_{pi} . The introduction of Lagrange multipliers in order to enforce the requirement of orthonormality of the $|\phi_i\rangle$, and variation of the C_{pi} lead to the HF-SCF-LCAO-MO equations

$$\vec{F} \vec{C}_i = \epsilon_i \vec{S} \vec{C}_i, \quad 1 \leq i \leq N/2 \quad (7)$$

where \vec{C}_i is a column vector with K components

$$\vec{C}_i = \begin{pmatrix} C_{1i} \\ \vdots \\ C_{Ki} \end{pmatrix}, \quad (8)$$

and \vec{S} is the overlap matrix with elements

$$S_{pq} = \langle \chi_p | \chi_q \rangle. \quad (9)$$

The Fock matrix, \vec{F} , has elements

$$F_{pq} = \langle \chi_p | h_1 + \sum_i (2J_i - K_i) | \chi_q \rangle, \quad (10)$$

where

$$h_1 = -\nabla^2/2 - \sum_{\alpha} Z_{\alpha}/|\vec{r}_1 - \vec{R}_{\alpha}| + \sum_{\alpha > \beta} Z_{\alpha} Z_{\beta}/|\vec{R}_{\alpha} - \vec{R}_{\beta}|, \quad (11)$$

the Coulomb operator is

$$J_i = \langle \phi_i(2) | r_{12}^{-1} | \phi_i(2) \rangle, \quad (12)$$

and the exchange operator is defined by

$$K_i | \chi_q \rangle = \langle \phi_i(2) | r_{12}^{-1} | \chi_q(2) \rangle | \phi_i \rangle. \quad (13)$$

The quantities ϵ_i are the molecular orbital single particle energies. The factor 2 arises in Eq. (10) because all states are doubly occupied in the closed shell system. Because the matrix elements of Eqs. (12) and (13) involve matrix elements over molecular orbitals, Equations (7) are, in fact, non-linear and of the third degree in the expansion coefficients C_{pi} .

Equations (7) have a deceptively simple appearance. Not only has the non-linearity of the problem been suppressed but also there is a vast number of two electron integrals to be evaluated. Neglecting possible reductions in the number of integrals due to molecular symmetry, there are

$$N_K = (K/4)(K+1) [(K/2)(K+1)+1]$$

distinct two-electron integrals for a K-dimensional basis set calculation of the F_{pq} . In the case of a molecule such as DMNA, a minimal basis set for only the valence electrons has 30 members and $N_{30}=108345!$ Many of these may be expected to be small, however, and this leads to the introduction of semi-empirical approximations.

III. SEMI-EMPIRICAL HF-SCF-LCAO-MO APPROXIMATIONS

Reducing the number of two-electron integrals that require evaluation simplifies the computation of the solutions of Eqs. (7). The most optimistic assumption about the matrix element

$$\begin{aligned} \int d\vec{r}_1 d\vec{r}_2 \chi_p^*(1) \chi_r^*(2) r_{12}^{-1} \chi_q(1) \chi_s(2) \\ \equiv (pq|rs) \end{aligned} \quad (14)$$

is that if either or both of (p,q) and (r,s) refer to different atomic orbitals, oscillations in the integrand due to differing nodal structures will cause the matrix element to be small. The zero differential overlap approximation then sets

$$\begin{aligned} (pq|rs) &= (pp|rr)\delta_{pq}\delta_{rs} \\ &= \gamma_{\alpha\beta}\delta_{pq}\delta_{rs} \quad (p,q) \in \alpha; (r,s) \in \beta \end{aligned} \quad (15)$$

Further approximations must be introduced in order to construct a theory invariant to unitary transformations of both the MO's and AO's⁵.

Two particular sets of approximations lead to the construction of the MINDO/3² and MNDO³ Hamiltonians, which however, have several common features. Both of them incorporate the assumption that a frozen core of inner shell electrons completely shields the bare nuclear charge. Similarly, only a minimal basis set of AO's is retained for the valence electrons; thus, hydrogen is represented by a single 1s orbital, and the remainder of the first row atoms are represented by the four orbitals 2s, 2p_x, 2p_y and 2p_z. The orbital exponents are adjusted from their usual values by treating them as parameters during the empirical determination of (pp|rr). Both models neglect all three and four center integrals, and presume that overlap matrix elements enter the wave function normalization matrix S as the unit matrix, but may differ from the unit matrix elsewhere. Monatomic differential overlap is retained for all one center integrals.

In MINDO/3² one-center, one-electron matrix elements are related to observed ionization potentials and spectroscopic data, as are the one-center two-electron repulsion integrals. The attractive integrals

between an electron centered on atom α and the core of a different atom β are assumed to depend only upon the pair of atoms involved, and are determined by a phenomenological form which reduces to the classical Coulomb attraction when $R_{\alpha\beta}$, the distance between atoms α and β , becomes large. The two-center core resonance integrals are assumed to be given by

$$S_{pr}(I_{\alpha} + I_{\beta})f(R_{\alpha\beta}), \quad (16)$$

where S_{pr} is the overlap between orbitals p and r centered on atoms α and β , respectively, $I_{\alpha(\beta)}$ is the ionization potential of atom $\alpha(\beta)$, and f is a function to be determined; in practice f is chosen to be a constant, $B_{\alpha\beta}$. The two-center two-electron repulsion integrals are required to be determined only by the atom pair α and β as a result of rotational invariance⁵, and are given by a form which tends to $R_{\alpha\beta}^{-1}$ for large $R_{\alpha\beta}$, and on the average of one-center two-electron integrals for atoms α and β when $R_{\alpha\beta} \rightarrow 0$. Finally, the core-core repulsions are determined by empirically fitting the parameters of an analytic formula.

The MNDO Hamiltonian³ extends and generalizes the MINDO/3 Hamiltonian. Matrix elements of the form

$$(pq|rs) \quad (p,q) \in \alpha, (r,s) \in \beta \quad (17)$$

are retained for $p \neq q$, $r \neq s$, and matrix elements of the form $(pp|rr)$ are allowed to depend not only on α and β but also upon the values of p and r . Nevertheless, matrix elements of the form $(pr|qs)$ are neglected as before. The one-center matrix elements are treated as in MINDO/3. The attractive integrals between an electron centered on atom α and the core of another atom β are calculated by assigning the quantum mechanical monopole

TABLE 6. Comparison of MNDO results with experimental data
for $\text{Cl}(\text{CH}_3)\text{N}(\text{NO}_2)$.

Observable	Experiment ^a	MNDO
$R(\text{NN})(\text{\AA})$	1.469 ± 0.005	1.434
$R(\text{NO})(\text{\AA})^b$	1.209 ± 0.002	1.206
$R(\text{CN})(\text{\AA})$	1.478 ± 0.005	1.492
$R(\text{C}\text{--}\text{N})(\text{\AA})$	1.720 ± 0.004	1.735
$\angle \text{CNN}(\text{\AA})$	112.9 ± 1.5	117.8
$\angle \text{C}\text{--}\text{N}\text{--}\text{N}(\text{\AA})$	108.4 ± 1.3	111.0
$\angle \text{C}\text{--}\text{N}\text{--}\text{C}(\text{\AA})$	115.0 ± 1.2	110.5
$\angle \text{CNO}(\text{\AA})$	128.5 ± 0.9	123.7
$\angle \text{C}\text{--}\text{N}\text{--}\text{NO}(\text{\AA})$	24.4 ± 1.0	50.7
$\angle \text{C}\text{--}\text{N}\text{--}\text{NO}(\text{\AA})$	27.0 ± 1.0	5.7
$\Delta H(\text{kcal m}^{-1})$		41.4
χ^2		128

^aRef. 9.

^bAverage value.

TABLE 5. Comparison of MNDO and MINDO/3 results with experimental data for $(\text{CH}_2\text{Cl})(\text{CH}_3)\text{N}(\text{NO}_2)$.

Observable	Experiment ^a	MNDO	MINDO/3
$R(\text{Å})^b$	1.426 ± 0.010	1.452	1.431
$R(\text{NO})(\text{Å})^c$	1.220 ± 0.003	1.208	1.238
$R(\text{CCl})(\text{Å})$	1.790 ± 0.007	1.814	1.940
$\angle \text{ONC}(\text{°})$	123.5 ± 0.5	123.3	123.4
$\angle \text{C}^5\text{NN}(\text{°})$	116.2 ± 0.5	118.2	117.5
$\angle \text{CNC}(\text{°})$	127.5 ± 0.5	117.8	109.1
$\angle \text{NCCl}(\text{°})$	112.3 ± 0.8	112.2	120.5
$\angle \text{C}^5\text{NNU}(\text{°})$	35.0 ± 1.0	-0.3	0.3
$\angle \Theta(\text{°})^d$	0 ± 1.0	22.1	-0.01
$\Delta H(\text{kcal m}^{-1})$		13.6	127.8
χ^2		240	398

^aRef. 9.

^b $\bar{R} = (1/3) [R(\text{C}^5\text{N}) + R(\text{C}^9\text{N}) + R(\text{NN})]$.

^cAverage value.

^dDiscussed in text.

TABLE 4. Comparison of MNDO and MINDO/3 with experimental data for $(\text{CH}_3)\text{N}(\text{NO}_2)_2$, a non-planar molecule.

Observable	Experiment ^b	MNDO	MINDO/3
$R(\text{NN})(\text{\AA})^a$	1.480 ± 0.005	1.437	1.355
$R(\text{NO})(\text{\AA})^a$	1.231 ± 0.003	1.203	1.219
$R(\text{CN})(\text{\AA})^a$	1.494 ± 0.006	1.502	1.460
$\angle \text{NNN}(\text{\AA})^a$	117.0 ± 1.1	113.2	122.7
$\angle \text{ONO}(\text{\AA})^a$	132.0 ± 1.0	125.4	132.3
$\angle \text{CNN}(\text{\AA})^a$	107.5 ± 1.0	114.6	121.4
$\angle \text{O}^4\text{N}^1\text{N}^2\text{N}^3(\text{\AA})^a$	0.1 ± 2.0	-29.8	67.8
$\angle \text{O}^5\text{N}^1\text{O}^4\text{N}^2(\text{\AA})^a$	$\pm 180.0 \pm 1.0$	174.1	-178.6
$\angle \text{O}^6\text{N}^3\text{N}^2\text{N}^1(\text{\AA})^a$	0.0 ± 2.0	113.2	19.0
$\angle \text{O}^7\text{N}^3\text{O}^1\text{N}^2(\text{\AA})^a$	$\pm 180.0 \pm 2.0$	-179.0	-177.3
$\angle \text{CN}^2\text{N}^3\text{N}^1(\text{\AA})^a$	42.2 ± 1.0	36.2	5.3
$\Delta H(\text{kcal m}^{-1})$		53.9	-36.4
χ^2		342	318

^aAverage value.

^bAll experimental data are from Ref. 15.

TABLE 3. Comparison of MNDO and MINDO/3 results with experimental data for $\text{H}(\text{CH}_3)\text{N}(\text{NO}_2)$.

Observable	Experiment ^a	MNDO	MINDO/3
$R(\text{NN})(\text{\AA})$	1.381 ± 0.006	1.403	1.297
$R(\text{NO})(\text{\AA})^b$	1.228 ± 0.003	1.209	1.230
$R(\text{CN})(\text{\AA})$	1.452 ± 0.006	1.479	1.423
$\angle \text{CNN}(\text{^\circ})$	109.0 ± 1.3	119.6	131.8
$\angle \text{ONO}(\text{^\circ})$	125.3 ± 1.0	123.7	131.5
$\angle \text{CNH}(\text{^\circ})$	119.0 ± 1.0	110.3	109.5
$\angle \text{CNN}(\text{^\circ})$	28 ± 1	35.8	0.052
$\Delta H(\text{kcal m}^{-1})$		18.8	-25.1
χ^2		39.9	205.0

^aRef. 14.

^bAverage value.

TABLE 2. Comparison of MNDO and MINDO/3 results with experimental data for $(\text{CH}_3)_2\text{N}(\text{N})_2$.

Observable	Experiment ^a	MNDO	MINDO/3
$R(\text{NN})(\text{\AA})$	1.382 ± 0.003	1.395	1.311
$R(\text{NO})(\text{\AA})^b$	1.223 ± 0.002	1.209	1.232
$R(\text{CN})(\text{\AA})^b$	1.460 ± 0.003	1.486	1.446
$R(\text{CH})(\text{\AA})^b$	1.121 ± 0.005	1.115	1.118
$\angle \text{ONO}(\text{^\circ})$	130.4 ± 1.5	122.8	130.2
$\angle \text{CNN}(\text{^\circ})$	116.2 ± 0.3	117.9	122.0
$\angle \text{C}^5\text{N}^2\text{N}^1\text{O}^3(\text{^\circ})$	0.0 ± 1.0^d	19.0	1.10
$\angle \text{C}^6\text{N}^2\text{N}^1\text{O}^3(\text{^\circ})$	180.0 ± 1.0^d	178.9	180.0
$\angle \text{O}^4\text{N}^1\text{N}^2\text{O}^3(\text{^\circ})$	180.0 ± 1.0^d	175.8	180.0
$\mu(\text{D})$	4.61 ± 0.06^e	4.51	4.19
$\Delta H(\text{kcal m}^{-1})$	-16.9 ± 1.0^f	22.9	-9.6
χ^2		210	98

^aAll experimental data are from Ref. 9 unless otherwise noted.

^bAveraged over all bonds.

^cRef. 10.

^dExperimental uncertainty assigned in the present work.

^eRef. 11.

^fRef. 12.

TABLE 1. Comparison of MNDO and MINDO/3 results with experimental data for $\text{H}_2\text{N}(\text{NO}_2)$.

Observable	Experiment ^a	MNDO	MINDO/3
$R(\text{NN})(\text{\AA})$	1.427 ± 0.002^b	1.406	1.287
$R(\text{NO})(\text{\AA})$	1.206 ± 0.01^c	1.209^b	1.230
$R(\text{NH})(\text{\AA})$	1.005 ± 0.010	1.018^b	1.027^b
$\angle \text{HNH}(\text{\AA})$	115.2 ± 2.0	107.4	108.3
$\angle \text{ONU}(\text{\AA})$	130.1 ± 0.25	124.1	132.2
$\angle \Phi(\text{\AA})$	51.8 ± 1.0	45.1	0.03
$\angle \Psi(\text{\AA})$	0 ± 0^d	5.8	0.00
$\Delta H(\text{kcal m}^{-1})$	-13.7 ± 1.0^e	19.4	-29.8
$\mu(\text{D})$	3.57 ± 0.05	3.84	3.95
χ^2		238	998

^aAll experimental data are from Ref. 7 unless otherwise noted.

^bAveraged over the two bonds.

^cAssumed value in Ref. 7. The uncertainty is assigned in the present work.

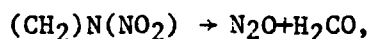
^dThe uncertainty is assigned in the present work.

^eRef. 8.

V. CONCLUSIONS

An HF-SCF-LCAO-MO study of several acyclical nitramine compounds has been performed in the MNDO and MINDO/3 approximations. The geometries predicted by MNDO tend to be better than those predicted by MINDO/3 for the pyramidal molecules, but this is not the case for planar molecules. The heats of formation predicted by MINDO/3 are in better agreement with experiment than those of MNDO. Application of both models to chlorinated, acyclical nitramines may be undertaken with caution.

Because of the success of MINDO/3 in accounting for the properties of the model compound DMNA, study of the reaction



which occurs in the decomposition of that model, may be undertaken with confidence in the results. Such calculations may be expected to lead to increased understanding of the dynamics of energetic materials.

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MINDO/3 fail to rotate the CNC plane with respect to the $N(NO_2)$ plane. This result is consistent with the tendency, observed in this work, of MINDO/3 to predict planar nitramines. The CCl bond length predicted by MNDO is in fair agreement with experiment while that predicted by MINDO/3 is rather large. The heats of formation predicted by both MNDO and MINDO/3 for $ClMMNA$ are both positive with the value yielded by the former similar to the others obtained in this work. It is the first such value obtained from MINDO/3 and suggests caution in applying the model to chlorinated nitramines.

F. N-chloro-N-methylnitramine - $Cl(CH_3)N(NO_2)$

Figure 8 contains a wedge diagram for N-chloro-N-methylnitramine ($ClMNA$), and Table 6 contains the comparison of experimental data with MNDO results. The MINDO/3 calculations for $ClMNA$ led to the dissociation of the system into NO_2 and $(CH_3)NCl$ fragments. The difficulty may lie with the Cl parameterization within MINDO/3. The structure predicted by MNDO, on the other hand, is in quite reasonable agreement with experiment. It is encouraging to observe that the ClN bond and $ClNN$ angle agree well with experiment. The torsions, $\angle CNNO$ and $\angle ClNNO$ are respectively smaller and larger than those observed. The calculated heat of formation is positive in agreement with the other MNDO values obtained in this study.

suggests the speculation that the value is negative which would be in agreement with the MINDO/3 prediction.

D. N-nitro-N-methyl nitramine - $(\text{NO}_2)(\text{CH}_3)\text{N}(\text{NO}_2)$

Figure 6 contains a wedge diagram illustrating the structure of N-nitro-N-methyl nitramine (dinitromethylamine; NMNA), and Table 4 contains a comparison of the results of the calculations with experiment. Experimentally, the two nitro groups and the N^1N^2 bond lie within a single plane, and the CN bond is displaced out of the plane. Both MNDO and MINDO/3 yield the result that the oxygen atoms are rotated out of the $\text{N}^1\text{N}^2\text{N}^3$ plane. The pyramidal location of the CN bond with respect to the plane of the nitrogen atoms is better reproduced by MNDO than by MINDO/3. In the present case, the NN bond length is more than 0.2\AA longer than in nitramide, a trend which is more closely followed by MNDO than by MINDO/3. The CN bond lengths appear to be insensitive, both experimentally and theoretically, to the other moiety bonded to the amino nitrogen atom. As in the previous cases, MNDO yields a positive heat of formation while MINDO/3 yields one that is negative.

E. Chloromethyl-methylnitramine - $(\text{CH}_2\text{Cl})(\text{CH}_3)\text{N}(\text{NO}_2)$

Figure 7 contains a wedge diagram for chloromethyl-methylnitramine (C α MMNA), and Table 5 contains the comparison between experiment and the results of the calculations. The bonds emanating from the amino nitrogen atom are rotated from the $\text{N}(\text{NO}_2)$ plane. In Table 5, the angle θ is defined to be the angle between the CNC and C^5NN planes. The MNDO calculation yields a result for this quantity that is in poor agreement with experiment, while MINDO/3 yields satisfactory agreement. Both MNDO and

the structural data have been obtained from electron diffraction.^{9,10} The third and fourth angles listed in the table are torsion angles defined according the IUPAC convention¹³, while the fifth angle may be considered to be the torsion for the N^2O^3 bond and the O^4N^1 "pseudo-bond". The MNDO results are slightly better than those obtained for nitramide, while those obtained from MINDO/3 are quite good. As before, the NN bond length yielded by MINDO/3 is appreciably shorter than that observed and may be understood in terms of the previously discussed population analysis. The dipole moment predicted by MNDO is in better agreement with experiment than that predicted by MINDO/3 principally as a result of the latter predicting a larger hybridization moment than the former. The heat of formation predicted by MNDO is 40 kcal m^{-1} too large and of the wrong sign, while that predicted by MINDO/3 is but 7 kcal m^{-1} too large and of the correct sign.

C. Methylnitramine - $H(CH_3)N(NO_2)$

There is some uncertainty about the location of the isolated H atom in methylnitramine (MNA)¹⁴, and Fig. 5 contains a Newman projection of the structure. The data and the results of the calculations are contained in Table 3. The NN bond length is approximately the same as in DMNA but 0.05A shorter than in nitramide. This trend is reproduced reasonably well by MNDO, but the NN bond length predicted by MINDO/3 is too short and does not exhibit this behavior. The CNNO torsion predicted by MNDO is larger than that observed while MINDO/3 yields a planar structure for the heavy atoms. Although the experimental value of the heat of formation of MNA is not known, consideration of $(CH_3)NO_2$, $H_2N(NO_2)$, and $(CH_3)_2N(NO_2)$

The two angles provide a measure of the agreement of the calculated and observed descriptions of the pyramidal structure of the molecule. The alternative of constraining the heavy atoms to be coplanar was rejected because this property should be a consequence of the theory.

The results of Table 1 indicate that MNDO provides a quite reasonable description of the geometry of nitramide, while that predicted by MINDO/3 is rather poor. The NN bond length predicted by MINDO/3 is much too short and the molecule is predicted to be planar. The short NN bond length can be understood in terms of the HF wave function. The MINDO/3 Hamiltonian results in there being a larger positive charge on the nitro-N atom and a smaller (larger magnitude) negative charge on the amino-N atom. The increased electrostatic attraction between these atoms leads to a shortening of the bond length.

The heat of formation predicted by MNDO is 33 kcal m^{-1} too large while that predicted by MINDO/3 is 16 kcal m^{-1} too small but of the correct sign. It is interesting to note that the total molecular energy of MNDO is deeper than that of MINDO/3. The differences between the heats of formation predicted by the two models is principally due to the electronic energies of the constituent atoms.

B. Dimethylnitramine - $(\text{CH}_3)_2\text{N}(\text{NO}_2)$

Table 2 contains a comparison of the results of the calculations and experiment for dimethylnitramine (DMNA). Figure 4 contains a schematic illustration of the heavy atoms in the molecule which is planar. Most of

where Q_i are the theoretical and experimental quantities of interest and ΔQ_i^{ex} is the uncertainty of the observed Q_i^{ex} ; the total number of compared quantities for a molecule is N . The quantity χ^2 differs from the frequently encountered statistical quantity χ^2 . No parameters are being adjusted in order to fit experiment, and the sum of the weights is not normalized to unity. Excellent agreement between theory and experiment for molecular geometries would be to within 0.01\AA for bond lengths and 1° for bond angles.

A. Nitramide - $\text{H}_2\text{N}(\text{NO}_2)$

Structural information about the most elementary nitramine compound, $\text{H}_2\text{N}(\text{NO}_2)$, has been obtained from x-ray scattering⁶ and microwave spectroscopy.⁷ The molecule is pyramidal and schematically illustrated in Fig. 3. Table 1 contains experimental data for the molecule and the results of calculations performed with the MINDO/3 and MNDO Hamiltonians.

The angle ϕ is defined experimentally to be the angle between the HNH and $\text{N}(\text{NO}_2)$ planes. It is not theoretically necessary for four points to lie in a plane, and this possibility was allowed in the geometry optimizations. Accordingly, the definition

$$\cos \phi = \frac{[\vec{R}(\text{N}^1\text{N}^2) \times \vec{R}(\text{N}^2\text{O}^1)] \cdot [\vec{R}(\text{N}^1\text{H}^1) \times \vec{R}(\text{N}^1\text{H}^2)]}{|\vec{R}(\text{N}^1\text{N}^2) \times \vec{R}(\text{N}^2\text{O}^1)| |\vec{R}(\text{N}^1\text{H}^1) \times \vec{R}(\text{N}^1\text{H}^2)|} \quad (23)$$

has been adopted. A second angle ψ has been defined by the relation

$$\cos \psi = \frac{[\vec{R}(\text{N}^2\text{O}^2) \times \vec{R}(\text{N}^2\text{O}^1)] \cdot [\vec{R}(\text{N}^1\text{N}^2) \times \vec{R}(\text{N}^2\text{O}^1)]}{|\vec{R}(\text{N}^2\text{O}^2) \times \vec{R}(\text{N}^2\text{O}^1)| |\vec{R}(\text{N}^1\text{N}^2) \times \vec{R}(\text{N}^2\text{O}^1)|} \quad (24)$$

features of electron correlation into a theory otherwise lacking the effects of such correlation.

There are interesting aspects of the calculation of the theoretical heat of formation of a compound defined by

$$\Delta H^{\text{mol}} = U_m - \sum_{\alpha} E_{\alpha}^{\text{el}} + \sum_{\alpha} \Delta H^{\alpha} \quad , \quad (20)$$

where the total molecular energy is U_m according to Eq. (2), the atomic electronic energy for isolated atom α is E_{α}^{el} , and ΔH^{α} is the heat of formation of free atom α from the element in its standard state. In both MINDO/3 and MNDO the ΔH^{α} are experimental quantities but the E_{α}^{el} are theoretical quantities calculated with two different sets of approximations. It is, therefore, possible to perform calculations in the two models which agree very well with each other for U_m but which yield quite different values for the experimentally accessible heat of formation. It is also possible that ΔH^{mol} is positive for a stable compound which illustrates that it should not be confused with the binding energy encountered in nuclear chemistry

$$B^{\text{nuc}} = E_{\text{tot}}^{\text{nuc}} - (ZM_p + NM_n)c^2. \quad (21)$$

In Eq. (21), the total nuclear energy is $E_{\text{tot}}^{\text{nuc}}$ for the nucleus consisting of Z protons of the mass M_p and N neutrons of mass M_n . The binding energy B^{nuc} is always negative for a stable system.

IV. RESULTS

The quality of the theoretical results when compared to experiment is measured by

$$X^2 = N^{-1} \sum_{i=1}^N \left[(Q_i^{\text{th}} - Q_i^{\text{ex}}) / \Delta Q_i^{\text{ex}} \right]^2 \quad , \quad (22)$$

electronic charge distribution to β . The two-center one-electron core resonance integrals are assumed to be given by

$$S_{pr}(\beta_p^\alpha + \beta_r^\beta)/2, \quad p \in \alpha; \quad r \in \beta \quad (18)$$

where β_p^α and β_r^β are adjustable parameters characteristic of the orbitals and their parent atoms. The two-center two-electron repulsion integrals are determined by a semi-empirical form based upon a multipole expansion of the integral in question. For first row atoms calculated with a minimal basis set, this implies that quadrupole-quadrupole interactions are the highest order encountered. This represents an improvement over MINDO/3 because the integrals now depend not only on the atom pair but also on the electronic angular momenta. The forms chosen, of course, yield the correct results for very large and for very small separations $R_{\alpha\beta}$. Finally, the core-core repulsion integrals are determined from the quantum mechanical monopole charge distributions of atoms α and β modified by empirically determined exponential functions.

The semi-empirical methods are parameterized by calculating the heats of formation, equilibrium geometries, and electrostatic dipole moments of a number of sagaciously chosen molecules. These calculations are repeated many times in the process of performing a non-linear least squares optimization of

$$Y^2 = \sum_{\ell} \left[Y_{\ell}(\text{calc.}) - Y_{\ell}(\text{obs.}) \right]^2 w_{\ell}^2, \quad (19)$$

where the Y_{ℓ} are the quantities in question, and the w_{ℓ}^2 are weights ascribed to the Y_{ℓ} . This procedure creates an inter-dependency among the parameters which, because they are empirically determined, incorporate some

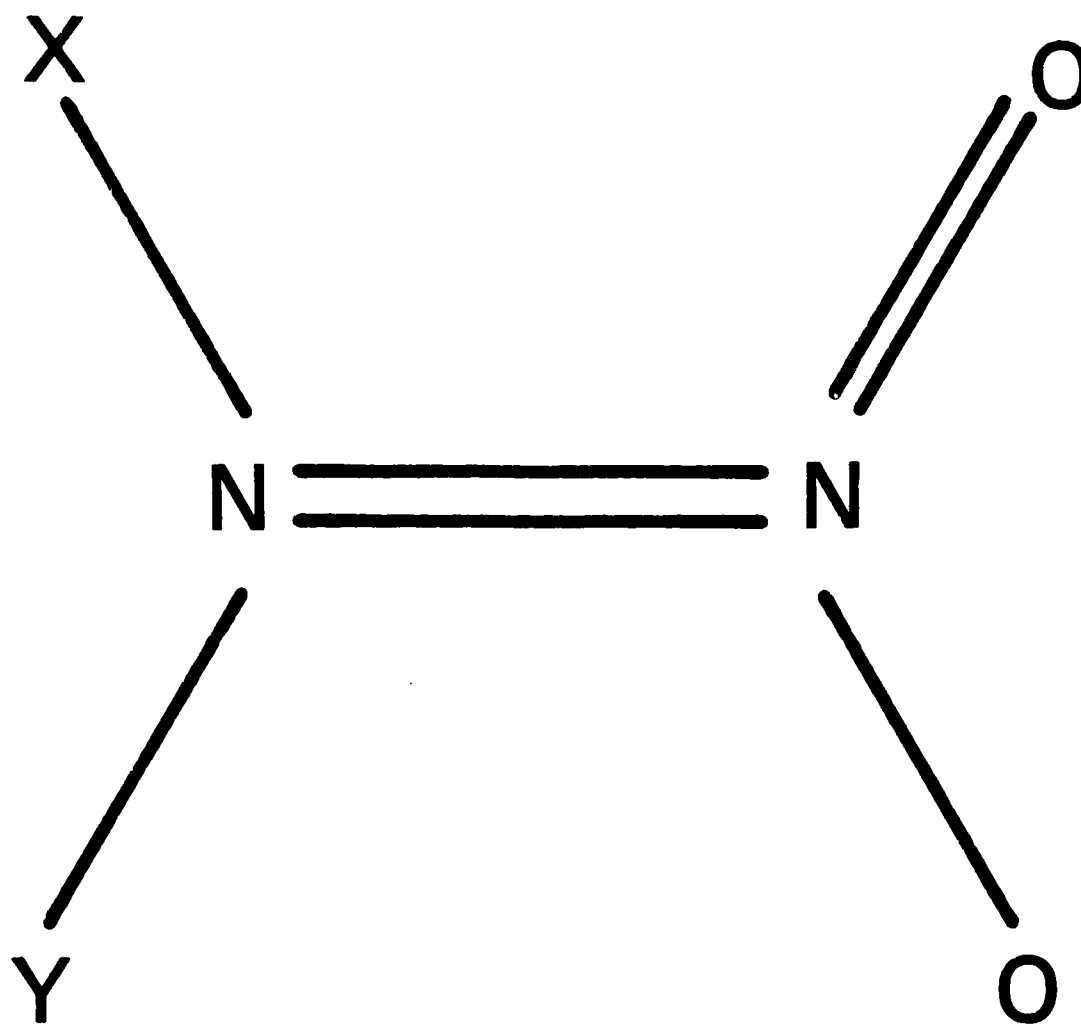
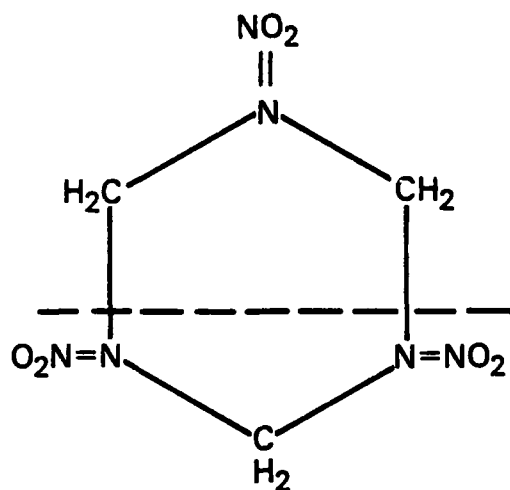
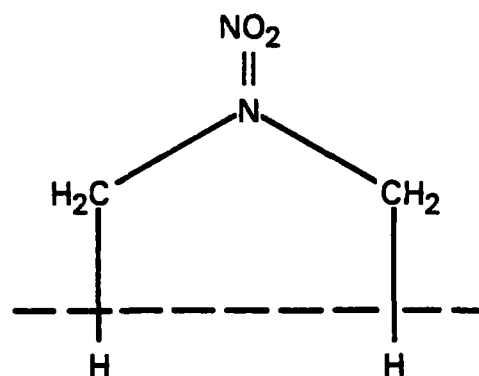


Fig. 1 Structural formula for a generic nitramine characterized by the N-NO₂ double bond. A resonance structure for the N-O bonds is understood, while the moieties X and Y may be members of a ring or radicals.



(a)



(b)

Fig. 2 (a) Structural formula of RDX, hexahydro - 1,3,5 trinitro-1,3,5 - triazine, an explosive.
(b) structural formula of dimethylnitramine, a model compound for RDX.

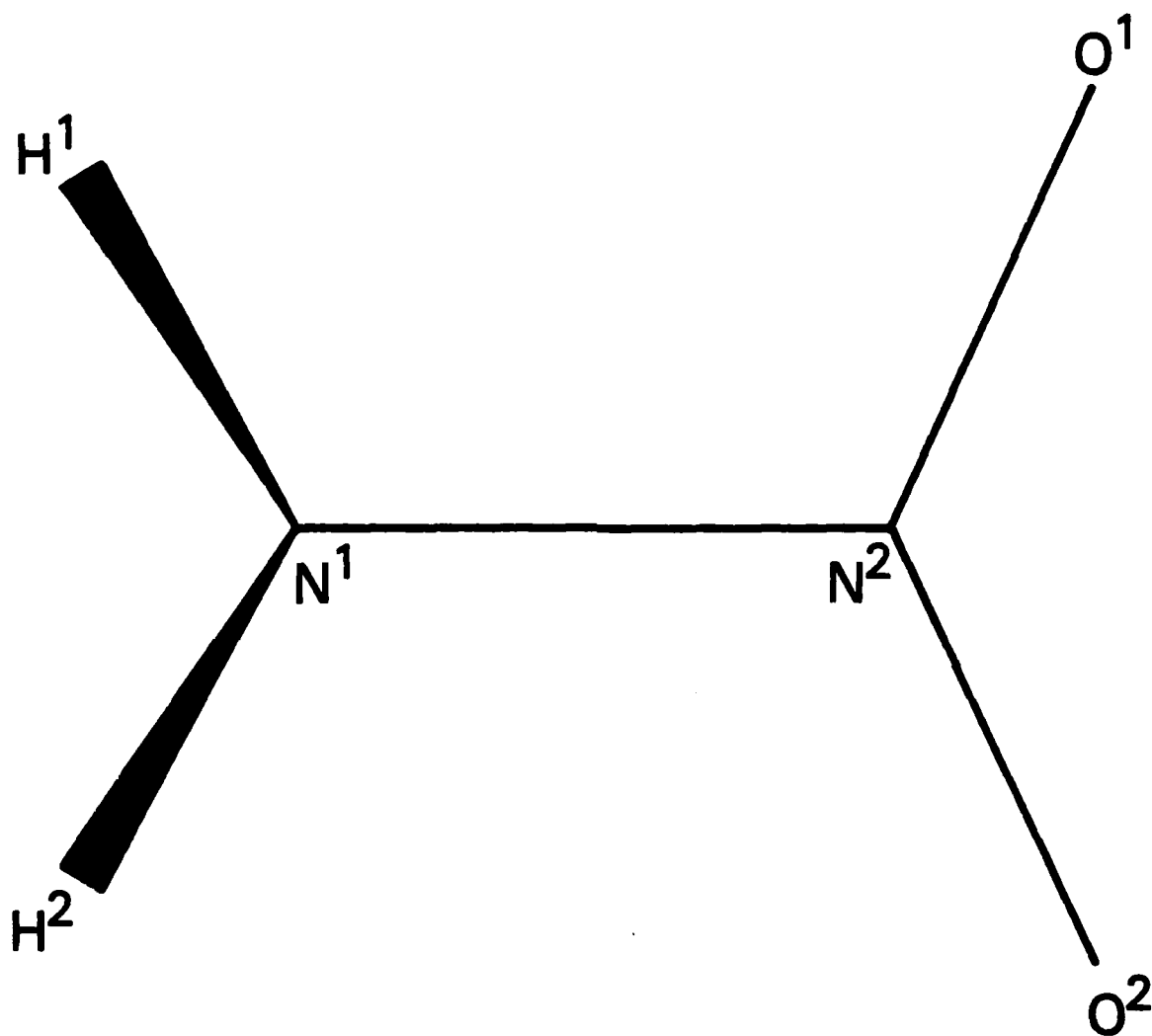


Fig. 3 Schematic illustration of $\text{H}_2\text{N}(\text{NO}_2)$. The angle between the HNH and $\text{N}(\text{NO}_2)$ planes is 51.8° .

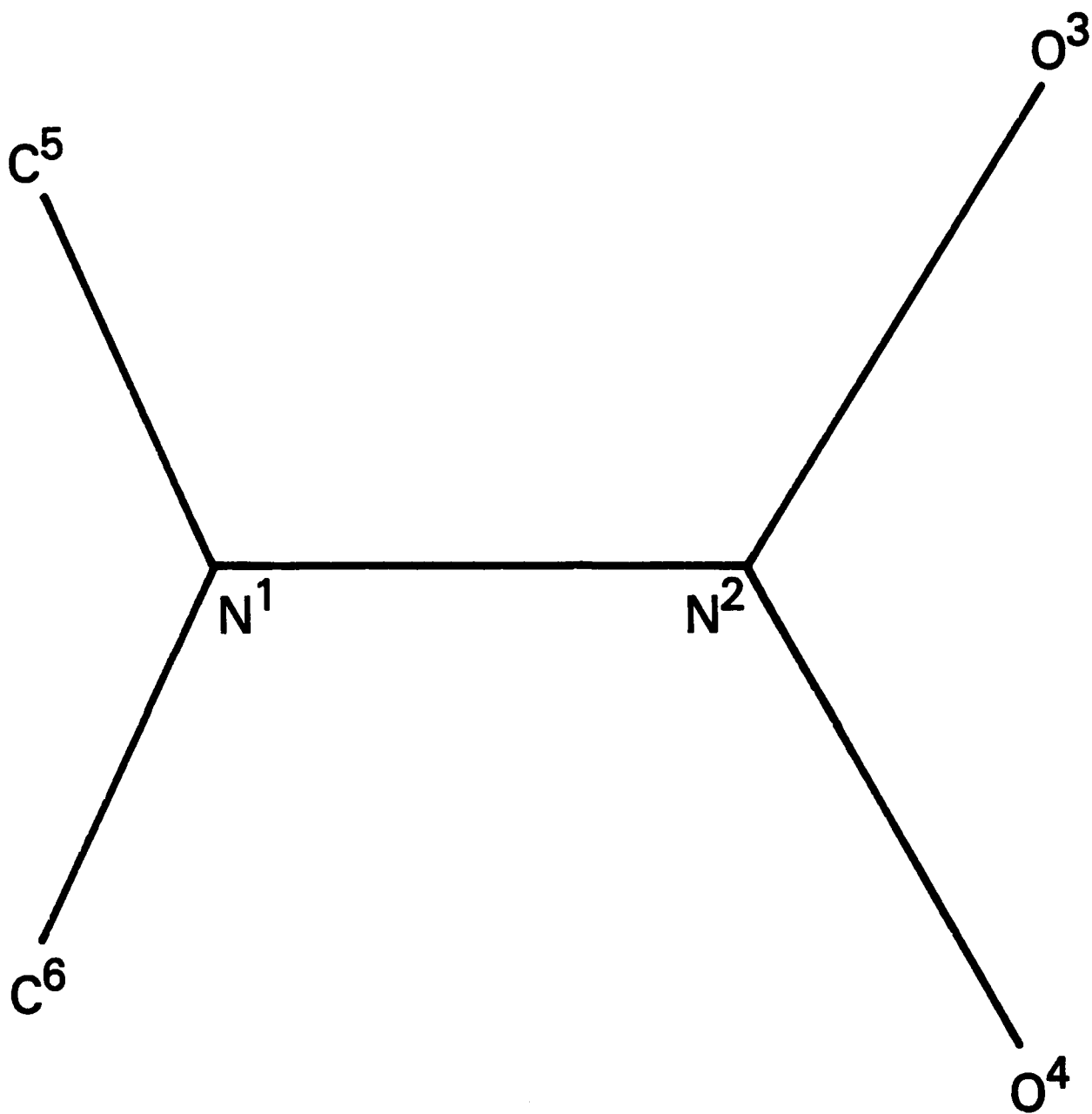


Fig. 4 Schematic illustration of $(\text{CH}_3)_2\text{N}(\text{NO}_2)$ for which the heavy atoms lie in a single plane.

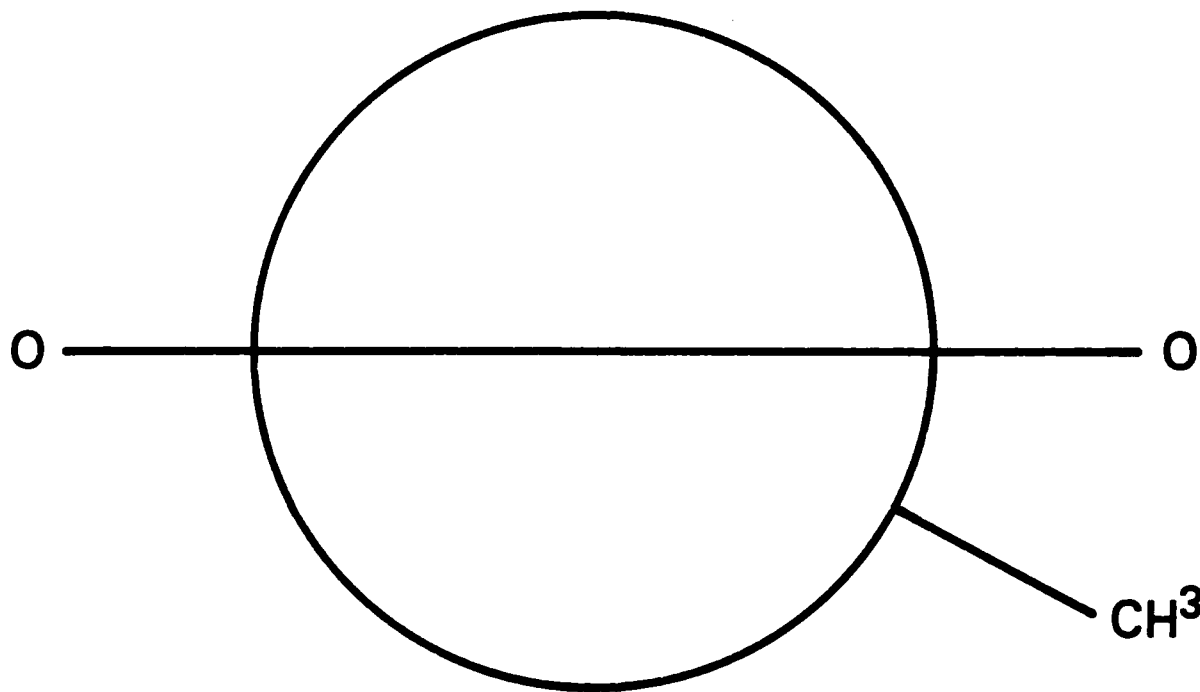


Fig. 5 Newman projection viewed along the axis from the nitro-N atom toward the amine-N atom for $\text{H}(\text{CH}_3)\text{N}(\text{NU}_2)$. The isolated H atom is not shown.

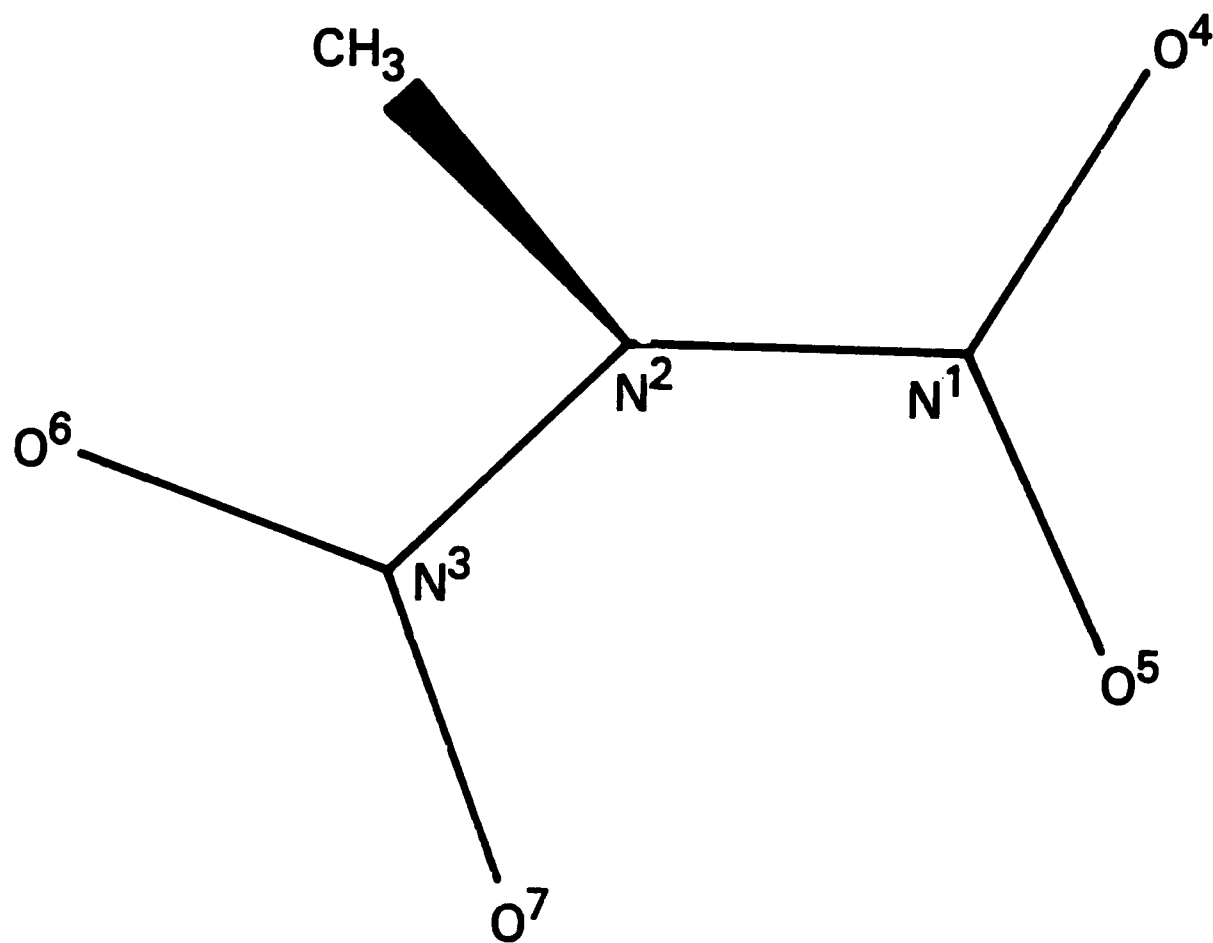


Fig. 6 Schematic illustration of N-nitro-N-methyl nitramine for which the nitro group and NN bond lie in a single plane while the CN bond is out of that plane.

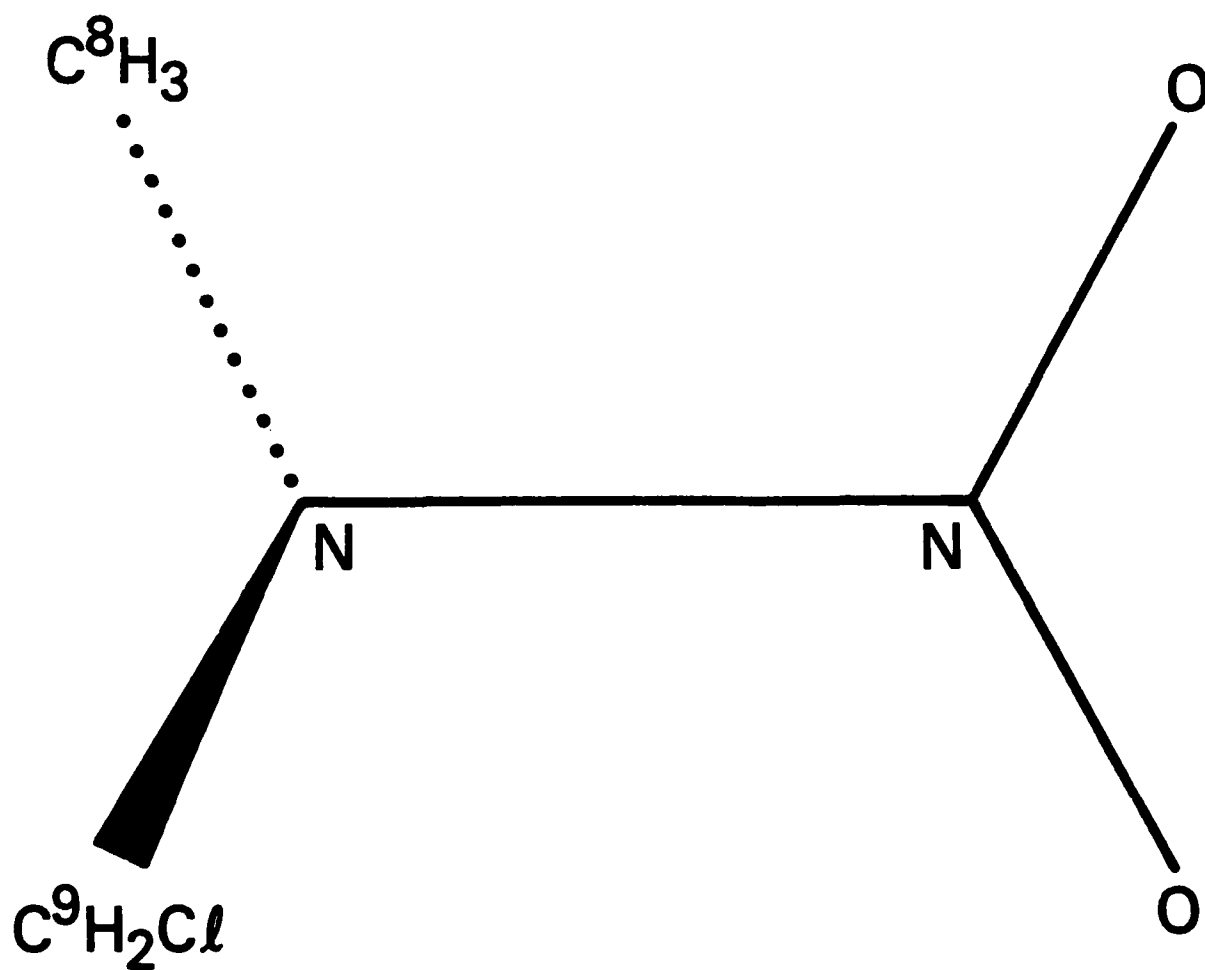


Fig. 7 Wedge diagram for the structure of (CH₂Cl)(CH₃)N(NO₂) for which the three bonds at the amine nitrogen atom lie in a single plane.

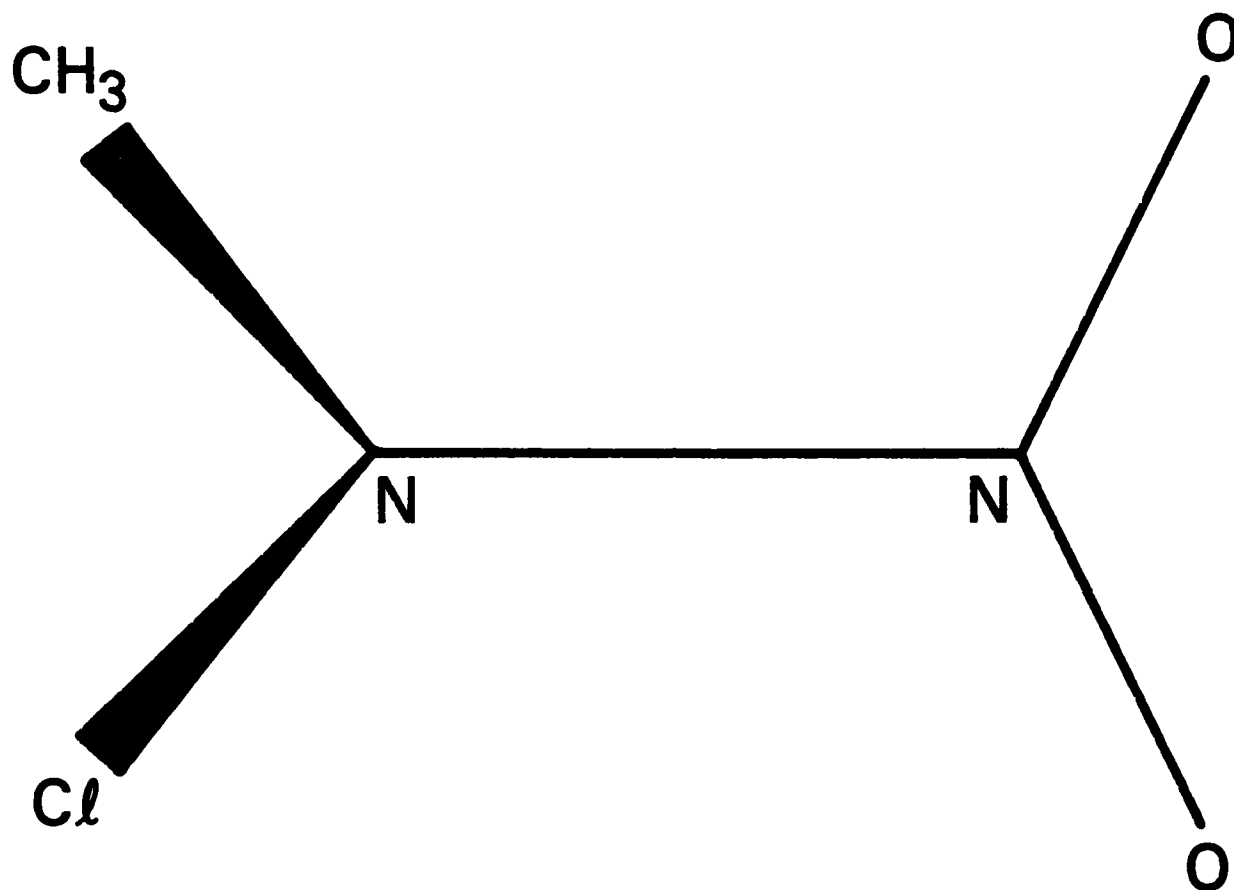


Fig. 8 Wedge diagram for the structure of $\text{Cl}(\text{CH}_3)\text{N}(\text{NO}_2)$ for which the bonds at the amine nitrogen atom are pyramidal.

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